

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-198523

(43)Date of publication of application : 24.07.2001

(51)Int.Cl.

B05D 7/14  
 B05D 1/28  
 B05D 7/24  
 B32B 15/08  
 C08G 73/10  
 H05K 3/00

(21)Application number : 2000-008870

(71)Applicant : MITSUI CHEMICALS INC

(22)Date of filing : 18.01.2000

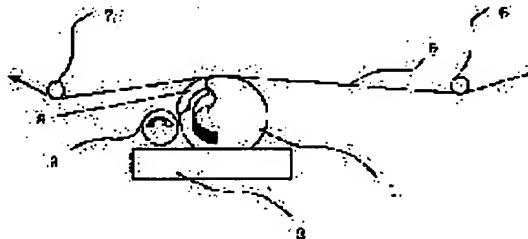
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## (54) METHOD OF MANUFACTURING FOR POLYAMIDE METALLIC FOIL LAMINATED BOARD

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a manufacturing method for polyamide metallic foil laminated board in which a coating liquid is uniformly applied without damaging the surface of metallic foil.

**SOLUTION:** In the manufacturing method for polyimide metallic foil laminated board obtained by applying the coating liquid of at least one selected from polyamide acid solution and polyamide solution on the surface of the metallic foil and heating to form a polyimide layer, the metallic foil is supported by 3 rollers of a front guide roll, a coat roll and a rear guide roll, the transferring quantity of the coating liquid to the coat roll is controlled with a metering roll and the coating liquid on the coat roll is transferred on the surface of the metallic foil by controlling the peripheral speed of the metering roll to 40-60% of the peripheral speed of the coat roll.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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## CLAIMS

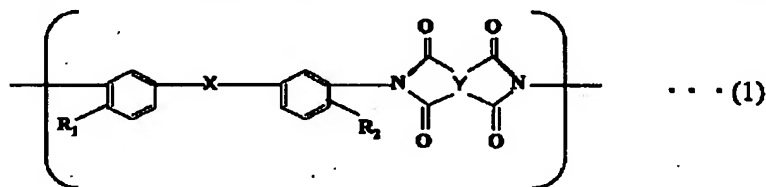
## [Claim(s)]

[Claim 1] In the manufacture approach of the polyimide metallic foil laminate which applies and heats a polyamide acid solution and at least one sort of coating liquid chosen from the polyimide solution on a metallic foil front face, and forms a polyimide layer in it This metallic foil is supported using three rolls, a pre-guide roll, a coat roll, and a post-guide roll. The manufacture approach of the polyimide metallic foil laminate characterized by controlling the amount of imprints of the coating liquid to a coat roll using a meta-ring roll, controlling the peripheral velocity of a meta-ring roll in 40 - 60% of range to the peripheral velocity of a coat roll, and imprinting the coating liquid on a coat roll to a metallic foil front face.

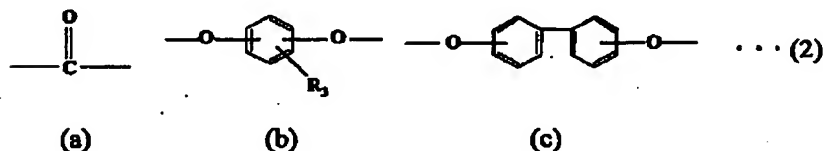
[Claim 2] The manufacture approach of the polyimide metallic foil laminate according to claim 1 characterized by drying in 50-300 degrees C, and subsequently imide-izing in 250-450 degrees C after imprinting coating liquid on a metallic foil front face.

[Claim 3] The manufacture approach of the polyimide metallic foil laminate according to claim 1 characterized by forming a polyimide layer with thermoplastic polyimide.

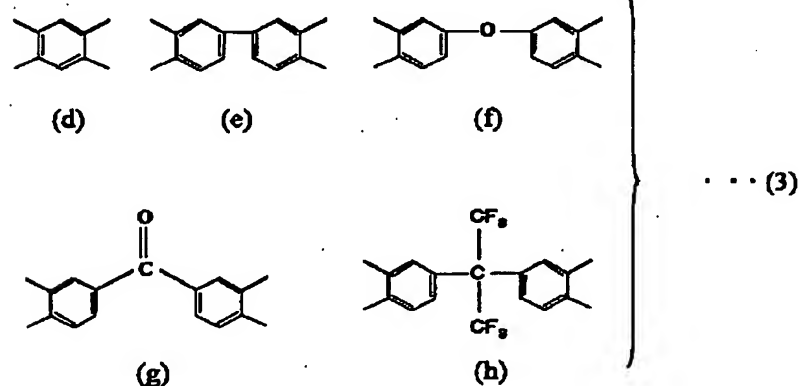
[Claim 4] thermoplastic polyimide — a general formula — (1 [-izing 1]) — [Formula 1]



(Inside of a formula, and X (a) of a general formula (2), (b), and (c) [-izing 2] [Formula 2])



since — one radical chosen from the becoming group — expressing — R1, R2, and R3 — respectively — independent — a hydrogen atom, a low-grade alkyl group, a low-grade alkoxyl group, a phenyl group, a biphenyl radical, a phenoxy group, a biphenoxy radical, a trifluoromethyl radical, a chlorine atom, or a bromine atom — expressing — Y — (d) of a general formula (3), (e), (f), (g), and (h) [-izing 3] — [Formula 3]



since — one radical chosen from the becoming group — being shown — the manufacture approach of the polyimide metallic foil laminate according to claim 3 characterized by being polyimide which has the repeat unit expressed.

[Claim 5] The manufacture approach of the polyimide metallic foil laminate according to claim 4 characterized by for

X in said general formula (1) being the radical of (a) of said general formula (2), or (b), and Y being the radical of (f) of said general formula (3), or (g).

[Claim 6] The manufacture approach of the polyimide metallic foil laminate according to claim 1 characterized by a metallic foil being copper foil.

[Claim 7] The manufacture approach of a polyimide metallic foil laminate according to claim 1 that thickness of a metallic foil is characterized by the thickness of each class of 5-150 micrometers and a polyimide layer being 0.1-10 micrometers.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a polyimide metallic foil laminate. In detail, it is related with the manufacture approach of the polyimide metallic foil laminate in which the homogeneity coating of coating liquid is possible.

[0002]

[Description of the Prior Art] Conventionally, the flexible metal polyimide laminate (it is called FMCL Flexible MetalClad Laminate and the following) has been widely used as an industrial ingredient by the thermal resistance, the electric insulation, and the mechanical characteristic which were excellent in polyimide resin. Although FMCL has the description which was excellent in versatility compared with other polymer laminates, the property for which FMCL is asked by advance of a technique is also developed, and, as for FMCL, it is desirable to have various engine performance according to an application.

[0003] In order to raise more especially the thermal resistance, the electric insulation, and the mechanical characteristic which were excellent in polyimide resin in recent years, the demand to the polyimide laminate whose polyimide layer is two-layer or a multilayer has been increasing. Moreover, on the other hand, the demand which makes thickness of polyimide thin from the degree of freedom of magnitude and processing of a printed-circuit board etc. is also high.

[0004] Then, FMCL which has a two-layer or multilayer polyimide layer needs to make at least one layer very thin, in order to make thickness of the whole polyimide layer thin. As the formation approach of a polyimide film with thin thickness, although extension of a film, coating, etc. are mentioned, since a glue line is minded when laminating, the property which was excellent in polyimide will be spoiled by extension of a film. Moreover, in shaping of the polyimide layer by coating, thickness nonuniformity becomes remarkable by making it thin. This is for a difference to arise in apparent average thickness and actual thickness.

[0005] When applying a polyimide solution etc. by the approach using the back up roll, and spreading thickness is thin, the smaller one of the gap of a base material and a coat roll is desirable to a skillful \*\*\*\*\* sake in an imprint. However, since there is deflection precision of a roll, the thickness nonuniformity for deflection precision of the back up roll and a coat roll occurs in fact. Moreover, the approach of forcing and applying to a coat roll so strongly that the back up roll being made distorted a little in order to cancel this thickness nonuniformity is also mentioned. On the other hand, surface preparation was performed to the spreading side front face for the purpose of adhesive improvement, when the external force by the back up roll etc. was added, the surface-preparation object might separate, and the metallic foil in recent years might lead to the fall of adhesive strength.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the manufacture approach of the polyimide metallic foil laminate in which the homogeneity coating of coating liquid is possible, without damaging the surface treatment of the polyimide spreading side of a metallic foil in view of the above-mentioned problem.

[0007]

[Means for Solving the Problem] Without using the back up roll in the coating process of coating liquid, as a result of inquiring wholeheartedly, by controlling the peripheral-velocity ratio of a meta-ring roll in the specific range, this invention persons made homogeneity the amount of the coating liquid of a coat roll surface, can imprint the coating liquid of uniform thickness to a metallic foil, found out that the above-mentioned technical problem could be solved, and resulted in this invention.

[0008] Namely, the summary of this invention is set to the manufacture approach of the polyimide metallic foil laminate which applies and heats a polyamide acid solution and at least one sort of coating liquid chosen from the polyimide solution on a metallic foil front face, and forms a polyimide layer in it. This metallic foil is supported using three rolls, a pre-guide roll, a coat roll, and a post-guide roll. The amount of imprints of the coating liquid to a coat roll is controlled using a meta-ring roll. It is the manufacture approach of the polyimide metallic foil laminate characterized by controlling the peripheral velocity of a meta-ring roll in 40 - 60% of range to the peripheral velocity of a coat roll, and imprinting the coating liquid on a coat roll to a metallic foil front face.

[0009] The manufacture approach of the polyimide metallic foil laminate in connection with this invention is usually the manufacture approach of the polyimide metallic foil laminate which dries in 50-300 degrees C, and is subsequently imide-ized in 250-450 degrees C, after imprinting coating liquid to a metallic foil front face.

[0010] In order to support a metallic foil in the coating process of coating liquid using three rolls, a pre-guide roll, a

coat roll, and a post-guide roll, according to this invention, without using the back up roll, the spreading side face of a metallic foil is not damaged. Moreover, since the coating liquid on a coat roll is made into homogeneity for the relative velocity of a meta-ring roll by controlling in the specific range, the coating of the uniform thickness of coating liquid is possible. Consequently, the thickness of the polyimide layer of the layered product obtained is uniform. Therefore, the polyimide metallic foil laminate manufactured by this invention is very useful in the electrician business field, the electronic industry field, etc. as a printed circuit board etc.

[0011]

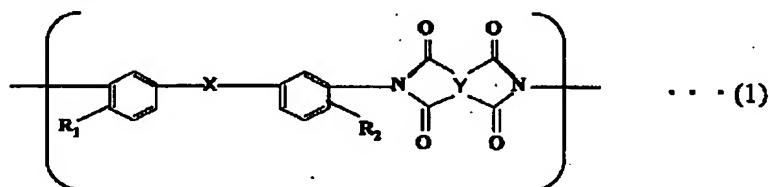
[Embodiment of the Invention] Hereafter, this invention is explained to a detail. This invention is the manufacture approach of the polyimide laminate which imprints the coating liquid on the coat roll controlled by the meta-ring roll by uniform thickness to up to a metallic foil in the spreading process which carries out coating of the polyamide acid which dissolved in the organic solvent, the polyimide, etc. on the metallic foil which is a base material, supporting a metallic foil with three rolls, a pre-guide roll, a coat roll, and a post-guide roll.

[0012] This invention has the description in controlling the peripheral velocity of a meta-ring roll to 40 - 60% of the peripheral velocity of a coat roll, and imprinting coating liquid. Usually, after imprinting coating liquid on a metallic foil front face, they are desiccation and the approach of imide-izing at specific temperature.

[0013] As a metallic foil which can be used for this invention, copper, softening aluminum, nickel, gold, silver, stainless steel, the alloy foil containing these, etc. are mentioned. Copper foil is [ among these ] desirable. The thickness of a metallic foil has desirable about 5-150 micrometers, when the total thickness of the whole layered product, flexibility, etc. are taken into consideration. Moreover, when it takes into consideration raising an adhesive property with a polyimide layer, and adhesion, it is desirable to perform surface treatment by adhesion processing of the metal particles by electrolytic plating, alternating current etching, etc.

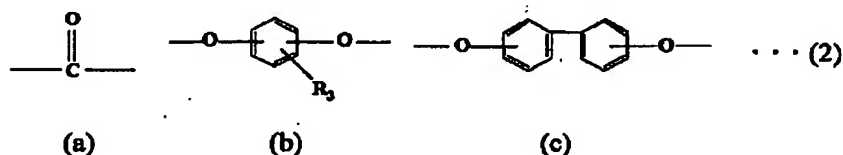
[0014] As for the polyimide layer concerning this invention, being formed with thermoplastic polyimide is desirable. As thermoplastic polyimide, it is general formula (1) [-ized 4] [0015].

[Formula 4]



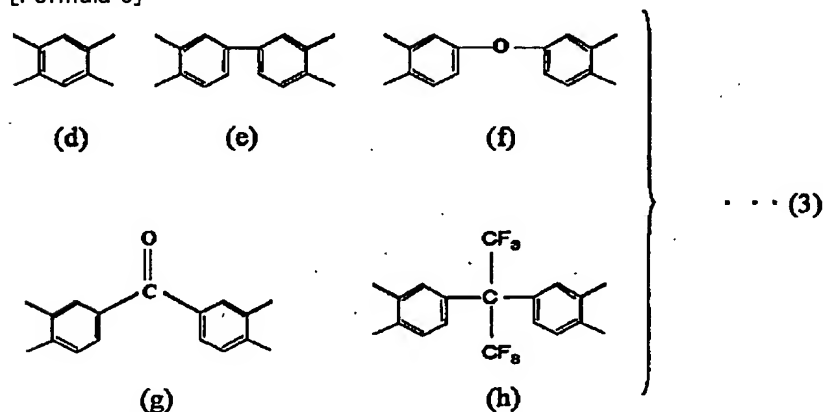
[0016] the inside of a formula, and X — (a) of a general formula (2), (b), and (c) — [-izing 5 [0017]]

[Formula 5]



[0018] since — one radical chosen from the becoming group — expressing — R1, R2, and R3 — respectively — independent — a hydrogen atom, a low-grade alkyl group, a low-grade alkoxyl group, a phenyl group, a biphenyl radical, a phenoxy group, a biphenoxy radical, a trifluoromethyl radical, a chlorine atom, or a bromine atom — expressing — Y — (d) of a general formula (3), (e), (f), (g), and (h) — [-izing 6 [0019]]

[Formula 6]



[0020] since — one radical chosen from the becoming group — being shown — it is desirable that it is polyimide which has the repeat unit expressed in a general formula (2), X is the radical of (a) or (b) — it is desirable.

Moreover, in a general formula (3), it is desirable that Y is the radical of (f) or (g).

[0021] The manufacture approach of the polyamide acid which is the thermoplastic polyimide which has the above-mentioned structure, or its precursor is described below. First, diamine is dissolved in an organic solvent in the container equipped with an agitator, a reflux cooler, and nitrogen installation tubing. Next, it adds so that it may become the 0.9-1.1-mol equivalent in this solution to diamine about aromatic series tetracarboxylic dianhydride under nitrogen-gas-atmosphere mind, and it agitates at 0-90 degrees C for 1 to 24 hours, and a polyamide acid solution is obtained. This polyamide acid solution is agitated at 100-200 degrees C, and a polyimide solution is obtained by carrying out reaction dehydration. Even if it dilutes these polyamide acid solutions and a polyimide solution with an organic solvent for viscosity accommodation, they do not interfere.

[0022] The above-mentioned polyamide acid or polyimide is compounded from diamine and tetracarboxylic dianhydride. As diamine which is a raw material, m-phenylenediamine, o-phenylenediamine, P-phenylene diamine, m-amino benzylamine, p-amino benzylamine, A screw (3-aminophenyl) sulfide, a sulfide (4(3-aminophenyl)-aminophenyl), A screw (4-aminophenyl) sulfide, a screw (3-aminophenyl) sulfoxide, A sulfoxide, a screw (3-aminophenyl) sulfone, (3-aminophenyl) (4-aminophenyl) A sulfone, a screw (4-aminophenyl) sulfone, (3-aminophenyl) (4-aminophenyl) A - diamino benzophenone, and 3 and 3' 3, 4'-diamino benzophenone, - diamino benzophenone, and 4 and 4' 3, 3'-diamino diphenylmethane, 3, - diamino diphenylmethane, and 4' 4, 4'-diamino diphenylmethane, - diamino diphenyl ether, and 4 and 4' 3, 3'-diamino diphenyl ether, 3, 4' - diamino diphenyl ether and screw [4-(3-amino phenoxy) phenyl] methane, Screw [4-(4-amino FENIKISHI) phenyl] methane, 1, and 1-screw [4-(3-amino phenoxy) phenyl] ethane, 1 and 1-screw [4-(4-amino phenoxy) phenyl] ethane, 1, 2-screw [4-(3-amino phenoxy) phenyl] ethane, 1 and 2-screw [4-(4-amino phenoxy) phenyl] ethane, 2, and 2-screw [4-(3-amino phenoxy) phenyl] propane, 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane, 2 and 2-screw [4-(3-amino phenoxy) phenyl] butane, 2, 2-screw [3-(3-amino phenoxy) phenyl]-1, 1, 1, 3 and 3, 3-hexafluoropropane, 2, 2-screw [4-(4-amino phenoxy) phenyl]-1, 1, 1, 3 and 3, 3-hexafluoropropane, 1, 3-screw (3-amino phenoxy) benzene, 1, 4-screw (3-amino phenoxy) benzene, 1, a - screw (4-amino phenoxy) benzene, and 4' 4, 4'-screw (3-amino phenoxy) biphenyl, 4 and 4' - screw (4-amino phenoxy) biphenyl and screw [4-(3-amino phenoxy) phenyl] ketone, A screw [4-(4-amino phenoxy) phenyl] ketone, a screw [4-(3-amino phenoxy) phenyl] sulfide, A screw [4-(4-amino phenoxy) phenyl] sulfide, a screw [4-(3-amino phenoxy) phenyl] sulfoxide, A screw [4-(amino phenoxy) phenyl] sulfoxide, a screw [4-(3-amino phenoxy) phenyl] sulfone, A screw [4-(4-amino phenoxy) phenyl] sulfone, the screw [4-(3-amino phenoxy) phenyl] ether, The screw [4-(4-amino phenoxy) phenyl] ether, 1, 4-screw [4-(3-amino phenoxy) benzoyl] benzene, 1, 3-screw [4-(3-amino phenoxy) benzoyl] benzene, 4 and 4' screw [ - ] [3-(4-amino phenoxy) benzoyl] diphenyl ether, 4 and 4' screw [ - ] [3-(3-amino phenoxy) benzoyl] diphenyl ether, 4 and 4' screw [ - ] [4-(4-amino - alpha and alpha-dimethylbenzyl) phenoxy] benzophenone, 4 and 4' screw [ - ] [4-(4-amino - alpha and alpha-dimethylbenzyl) phenoxy] diphenylsulfone, A screw [4-(4-(4-amino phenoxy) phenoxy) phenyl] sulfone, 1 and 4-screw [4-(4-amino phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1, and 3-screw [4-(4-amino phenoxy)-alpha and alpha-dimethylbenzyl] benzene etc. is mentioned.

[0023] the above — diamine — inside — desirable — p-phenylene diamine — three — three — ' - diamino — a benzophenone — four — four — ' - diamino — a benzophenone — one — three - a screw (3-amino phenoxy) — benzene — four — four — ' - a screw (3-amino phenoxy) — a biphenyl — and — a screw — [ - four - (3-amino phenoxy) — phenyl — ] — a sulfone — it is . Furthermore, it is a 1, 3-screw (3-amino phenoxy) benzene and 3, and 3'-diamino benzophenone preferably. Diamine is independent or may be used combining two or more sorts. Usually, as long as it is less than [ of the above mentioned diamine / 50 mol % ], you may substitute with other amine compounds.

[0024] As tetracarboxylic dianhydride, for example Ethylene tetracarboxylic dianhydride, Butane tetracarboxylic dianhydride, cyclopentane carboxylic-acid 2 anhydride, Pyromellitic acid 2 anhydride, 2, 2', 3, 3'-benzophenone tetracarboxylic dianhydride, - benzophenone tetracarboxylic dianhydride, 2, 2', and 3, 3', 4, and 4' 3, 3'-biphenyl tetracarboxylic dianhydride, - biphenyl tetracarboxylic dianhydride, and 3, 3', 4, and 4' 2, 2'-screw (3, 4-dicarboxy phenyl) propane 2 anhydride, Screw (3, 4-dicarboxy phenyl) ether 2 anhydride, screw (2, 3-dicarboxy phenyl) ether 2 anhydride, Screw (3, 4-dicarboxy phenyl sulfone) 2 anhydride, screw (2, 3-dicarboxy phenyl) sulfone 2 anhydride, 1 and 1-screw (2, 3-dicarboxy phenyl) methane 2 anhydride, screw (3, 4-dicarboxy phenyl) methane 2 anhydride, - (p-phenylene dioxy) JIFUTARU acid 2 anhydride and 4 and 4' 4, 4'-(m-phenylene dioxy) JIFUTARU acid 2 anhydride, 2, 3, 6, 7-naphthalene tetracarboxylic dianhydride, 1, 4 and 5, 8-naphthalene tetracarboxylic dianhydride, 1, 2, 5, 6, - naphthalene tetracarboxylic dianhydride, 1, 2 and 3, 4-benzene tetracarboxylic dianhydride, 3, 4, 9, 10-perylene tetracarboxylic dianhydride, 2, 3 and 6, 7-anthracene tetracarboxylic dianhydride, 1, 2 and 7, 8-phenanthrene tetracarboxylic dianhydride, etc. are mentioned.

[0025] They are - benzophenone tetracarboxylic dianhydride, 2, 2', and pyromellitic acid 2 anhydride, 2, 2', 3, 3'-benzophenone tetracarboxylic dianhydride, 3, 3', 4, and 4' 3, 3'-biphenyl tetracarboxylic dianhydride, 3, and 3' 4, 4'-biphenyl tetracarboxylic dianhydride and 1, 2 and 3, and 4-benzene tetracarboxylic dianhydride preferably among the above-mentioned tetracarboxylic dianhydride. Furthermore, they are 3, 3'4, and - biphenyl tetracarboxylic dianhydride and 3, 3', and 4' 4, 4'-benzophenone tetracarboxylic dianhydride preferably. Tetracarboxylic dianhydride can be used combining independent or two sorts or more.

[0026] A dicarboxylic acid anhydride may be added as a purpose which closes the polymer end of the thermoplastic polyimide concerning the thermoplastic polyimide layer of this invention. As a dicarboxylic acid anhydride used, phthalic anhydride, 2, 3-benzophenone dicarboxylic acid anhydride, 3, 4-benzophenone dicarboxylic acid anhydride, 2, a 3-dicarboxy phenyl phenyl ether anhydride, 2, 3-biphenyl dicarboxylic acid anhydride, 3, 4-biphenyl dicarboxylic

acid anhydride, 2, a 3-dicarboxy phenyl phenyl sulfone anhydride, 3, a 4-dicarboxy phenyl phenyl sulfone anhydride, 2, a 3-dicarboxy phenyl phenyl sulfide anhydride, 1, 2-North America Free Trade Agreement range KAROBON acid anhydride, 2, 3-naphthalene dicarboxylic acid anhydride, 1, 8-naphthalene dicarboxylic acid anhydride, 1, 2-anthracene dicarboxylic acid anhydride, 2, 3-anthracene dicarboxylic acid anhydride, 1, and 9-anthracene dicarboxylic acid anhydride is mentioned. These dicarboxylic acid anhydrides may be permuted by the radical which does not have an amine or a dicarboxylic acid anhydride, and reactivity. The additions of a dicarboxylic acid anhydride are usually the range of 0.001-0.5 mols, and range which is 0.005-0.25 mols preferably to the total quantity of 100 mols of the diamine which is the main raw material, and tetracarboxylic dianhydride.

[0027] Similarly, monoamine may be added in order to close the polymer end of thermoplastic polyimide. The following is mentioned as monoamine used. For example, an aniline, ortho toluidine, meta toluidine, para toluidine, 2, 3-xylidine, 2,4-xylidine, 2, 5-xylidine, 2, 6-xylidine, 3,4-xylidine, 3, 5-xylidine, o-chloroaniline, m-chloroaniline, p-chloroaniline, ortho nitroaniline, o-BUROMO aniline, m-BUROMO aniline, Ortho nitroaniline, meta nitroaniline, para nitroaniline, ortho aminophenol, m-aminophenol, para aminophenol, o-ANIRIJIN, m-ANIRIJIN, p-ANIRIJIN, o-phenetidine, m-phenetidine, p-phenetidine, o-amino Benz aldehyde, m-amino Benz aldehyde, p-amino Benz aldehyde, o-amino benzonitrile, m-amino benzonitrile, p-amino benzonitrile, 2-amino biphenyl, 3-amino biphenyl, 4-aminobiphenyl, 2-aminophenol phenyl ether, 3-aminophenol phenyl ether, 4-aminophenol phenyl ether, 2-amino benzophenone, 3-amino benzophenone, 4-amino benzophenone, 2-aminophenol phenyl sulfide, 3-aminophenol phenyl sulfide, 4-aminophenol phenyl sulfide, 2-aminophenol phenyl sulfone, 3-aminophenol phenyl sulfone, 4-aminophenol phenyl sulfone, alpha-naphthylamine, beta-naphthylamine, 1-amino-2-naphthol, a 2-amino-1-naphthol, a 4-amino-1-naphthol, A 5-amino-1-naphthol, a 5-amino-1-naphthol, 5-amino-2-naphthol, 7-amino-2-naphthol, 8-amino-2-naphthol, 1-amino anthracene, 2-amino anthracene, 9-amino anthracene, etc. are mentioned.

[0028] These monoamines are independent, or they may be used, combining them two or more sorts. The additions of monoamine are usually the range of 0.001-0.5 mols, and range which is 0.005-0.25 mols preferably to a total of 100 mols of the diamine which is the main raw material, and tetracarboxylic dianhydride.

[0029] As for the above-mentioned polyimide solution or the concentration of the precursor solution, in consideration of spreading nature etc., about 5 - 25% of the weight of an object is usually used. As an organic solvent, a N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, 1,3-dimethyl-2-imidazolidinone, N and N-dimethyl methoxy acetamide, dimethyl sulfoxide, a pyridine, A dimethyl sulfone, hexa methyl sulfo RUAMIDO, tetramethylurea, N-methyl caprolactam, a butyrolactam, a tetrahydrofuran, m-dioxane, para dioxane, 1, 2-dimethoxyethane, bis-2-(2-methoxyethoxy) ethyl ether, The solvent containing 1, 3-dioxane, 1, 4-dioxane, o-cresol, m-cresol, p-cresol, Cresylic acid, p-chlorophenol, an anisole, etc. is raised. A N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and N,N-dimethylformamide are mentioned preferably.

[0030] The coating approach of coating liquid for a metallic foil is explained. In the conventional roll coater, as shown in [ drawing 1 ], the coating liquid in the varnish pan 2 lifted with the coat roll 1 is measured by the meta-ring roll 3, and is imprinted and applied to the metallic foil 5 on the back up roll 4.

[0031] In a kiss mold reverse roll coater, as shown in [ drawing 2 R> 2], the coating liquid in the varnish pan 2 lifted with the coat roll 1 is measured by the meta-ring roll 3, and is imprinted and applied to the metallic foil 5 currently supported by three persons of the coat roll 1, the pre-guide roll 6, and the post-guide roll 7.

[0032] In this invention, since the back up roll 4 as shown in [ drawing 1 ] does not use it, a metallic foil 5 does not damage it, even if it is not pinched by the coat roll 1 and the back up roll 4 and surface treatment etc. is performed to the metallic foil. The coating side of coating liquid can be held flat and smooth.

[0033] The peripheral velocity of the meta-ring roll 3 in a coating process is controlled by this invention to 40 - 60% of the peripheral velocity of the coat roll 1. At less than 40%, unevenness arises in the shape of stripes in a flow direction. If it exceeds 60%, wave-like unevenness will occur crosswise. The thickness unevenness of a polyimide layer occurs in these condition.

[0034] In a spreading process, the coat roll 1 and the metallic foil currently supported by three persons of the guide rolls 6 and 7 of two approximately are the include angles won to the coat roll 1, and, as for the winning include angle of the metallic foil to a coat roll, it is desirable to hold in the range of 1 - 180 degrees. As for the tension of a base material, in a spreading process, it is desirable to hold in the range of 0.0020 - 0.1471 N/m. In the tension range exceeding 0.1471 N/m, a wrinkling occurs in a metallic foil and there is an inclination for a metallic foil to stop contacting a coat roll crosswise at homogeneity, in the range with which 0.0020 N/m is not filled.

[0035] As for the coating thickness of coating liquid, it is desirable that the thickness of each class of the polyimide layer after imide-izing is set to 25 micrometers or less. Furthermore, it is 0.2-10 micrometers preferably. A polyimide layer may be formed more than two-layer. Although there is especially no limit in the upper limit of a number of layers, they are usually about three layers.

[0036] As the desiccation approach, well-known approaches, such as roll support conveyance and the Ayr float conveyance, are conventionally employable. Usually, desiccation is dried to the range where a solvent content does not exceed the 150 weight sections to the polyimide 100 weight section under 50-300-degree C air or nitrogen-gas-atmosphere mind.

[0037] Although a well-known approach is used also with the batch method according [ the imide-ized approach after desiccation ] to inert oven, or the continuous system at an imide-ized furnace and there is especially no limit in the approach and conditions, it is the continuous system at an imide-ized furnace preferably. Usually, imide-ization is performed at 250-450 degrees C, and it imide-izes to the range where a solvent content does not exceed the 0.5 weight section to the polyimide 100 weight section.

[0038] The total thickness is about 15–200 micrometers, and the polyimide metallic foil laminate of this invention manufactured as mentioned above is used in the electrician business field, the electronic industry field, etc. as a printed circuit board etc.

[0039]

[Example] Next, the example of this invention is shown. However, this invention is not limited to the following examples at all. In addition, the coating nonuniformity shown in the example and a coating thickness difference were measured by the following approach.

[0040] (1) Carry out visual observation continuously and evaluate like the next the location (eight sections of drawing 2) before the coating liquid measured by the coating nonuniformity meta-ring roll on the coat roll is imprinted by the metallic foil. Those with nonuniformity: The lengthwise line or the wave pattern has occurred. Those without nonuniformity: The lengthwise line and the wave pattern have not occurred.

(2) Coating thickness difference (micrometer)

From the created sample, it starts in full x10cm magnitude, chemical etching processing is performed to a metallic foil layer using a ferric-chloride water solution (40wt%), and only a polyimide layer is obtained. Ten-point thickness is measured crosswise at equal intervals using a contact process thickness gage (the product made from HEIDENHAIN, formal:200068G). The difference of maximum and the minimum value is defined as a thickness difference.

[0041] the container equipped with example 1 agitator, a reflux cooler, and nitrogen installation tubing — 1 and 3-screw (3-amino phenoxy) benzene [APB] — 570g (1.95 mols), 3, and 3' — 4 and 4'-biphenyl tetracarboxylic dianhydride [BPDA]588g (2.0 mols) were dissolved in N,N-dimethylacetamide so that it might become 19wt(s)%. It agitated at 40 degrees C for 6 hours, and the polyamide acid solution was obtained. In 25 degrees C, the viscosity of this solution was 300 mPa-s. Travel-speed 5 m/min of a metallic foil is received using a kiss mold reverse roll coater as shown in [ drawing 2 ]. Peripheral velocity of 5.5 m/min (110%) and a meta-ring roll is made into 2.75 m/min (55%) for the peripheral velocity of a coat roll. The slack over metallic foil width of face imprinted and applied on the copper foil (an aurin company copper-metallurgy foil, a trade name: C7025, thickness of 18 micrometers, width of face of 68.4cm) which is 6.0mm so that the thickness after imide-izing might be set to 2 micrometers. The tension of copper foil of the winning angle to the coat roll of copper foil was 0.01471Ns/m 14 degrees. This polyamide acid coating copper foil was dried until a solvent content became the 5.0 weight sections to the resin solid content 100 weight section at 100 degrees C at a hot-air-drying furnace. Furthermore, it heated for 20 minutes and was made to imide-ize in 350-degree C nitrogen-gas-atmosphere mind (oxygen density 1 capacity %). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0042] the container equipped with example 2 agitator, a reflux cooler, and nitrogen installation tubing — 3 and 3'-diamino benzophenone [3, 3'-DABP] — 416g (1.96 mols), 3, and 3' — 4 and 4'-benzophenone tetracarboxylic dianhydride [BTDA]644g (2.0 mols) were dissolved in N,N-dimethylacetamide so that it might become 15wt(s)%. It agitated at 40 degrees C for 6 hours, and the polyamide acid solution was obtained. In 25 degrees C, the viscosity of this solution was 300 mPa-s. Metallic foil travel-speed 5 m/min is received using a kiss mold reverse roll coater as shown in [ drawing 2 ]. Peripheral velocity of 9.25 m/min (185%) and a meta-ring roll is made into 5.25 m/min (105%) for the peripheral velocity of a coat roll. The slack over metallic foil width of face imprinted and applied on the copper foil (an aurin company copper-metallurgy foil, a trade name: C7025, thickness of 18 micrometers, width of face of 68.4cm) which is 6.0mm so that the thickness after imide-izing might be set to 0.2 micrometers. The tension of copper foil of the winning angle to the coat roll of copper foil was 0.01471Ns/m 14 degrees. This polyamide acid coating copper foil was dried until a solvent content became the 5.0 weight sections to the resin solid content 100 weight section at 100 degrees C at a hot-air-drying furnace. Furthermore, it heated for 20 minutes and was made to imide-ize in 350-degree C nitrogen-gas-atmosphere mind (oxygen density 1 capacity %). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0043] The polyimide metal laminate was obtained like the example 1 except having made peripheral velocity of an example of comparison 1 meta-ring roll into 4 m/min (80%). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0044] The polyimide metal laminate was obtained like the example 1 except having made relative velocity of an example of comparison 2 meta-ring roll into 2 m/min (40%). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0045] The polyimide metal laminate was obtained like the example 2 except having made peripheral velocity of an example of comparison 3 meta-ring roll into 6.5 m/min (130%). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0046] The polyimide metal laminate was obtained like the example 2 except having made relative velocity of an example of comparison 4 meta-ring roll into 3.4 m/min (68%). The result of a coating thickness difference and coating nonuniformity is shown in [Table 1].

[0047]

[Table 1]



	Cロール周速度 (m/min)	M/C速度比 (%)	塗工ムラ	塗工厚み差 ( $\mu$ m)
実施例 1	5.5	50	無し	0.3
実施例 2	9.25	57	無し	—
比較例 1	5.5	73	有り (波)	0.7
比較例 2	5.5	36	有り (縦縞)	0.5
比較例 3	9.25	70	有り (波)	—
比較例 4	9.25	37	有り (縦縞)	—

[0048] Explanation of [Table 1]. C roll: Coat roll. M/C velocity ratio: The ratio of the peripheral velocity of the meta-ring roll to the peripheral velocity of a coat roll.

[0049]

[Effect of the Invention] As explained above, in case the polyamide acid or polyimide which dissolved in the organic solvent is made to imprint from on a coat roll to up to a metallic foil, without using the back up roll, supporting a metallic foil using three rolls, a pre-guide roll, a coat roll, and a post-guide roll, in a coating process, coating of this invention can be carried out without coating unevenness by controlling the peripheral velocity of a meta-ring roll in the specific range. Consequently, the thickness of the polyimide layer of the layered product obtained is uniform. Therefore, the polyimide metallic foil laminate manufactured by this invention is very useful in the electrician business field, the electronic industry field, etc. as a printed circuit board etc.

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[Translation done.]